α-Carbon–Sulfur Oxidation–Reduction Reactions of Sulfoxides. The Case of Benzylic Sulfoxides[1]

Derek A. Davenport,

Department of Chemistry, Purdue University, West Lafayette, Indiana

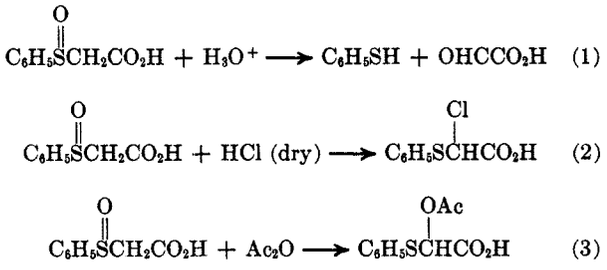
David B. Moss, Joseph E. Rhodes, and James A. Walsh[2]

Department of Chemistry, John Carroll University, Cleveland, Ohio

Received July 1, 1968

In refluxing glacial acetic acid, α-(benzylsulfinyl)-*p*-nitrotoluene (**1**) readily gives α,α-di(benzylthio)-*p*-nitrotoluene (**2**) and *p*-nitrobenzaldehyde (**4**), while benzyl sulfoxide (**6**) and phenyl benzyl sulfoxide (**8**) are unreactive. In contrast, **1**, **6**, and **8** all undergo redox reactions with hydrogen chloride in dry ether or alcohol. Isotope dilution analysis shows that, with hydrogen chloride in ether, **1** forms both **2** and α,α-di(*p*-nitrobenzylthio)toluene (**3**) in comparable amounts. Dimethyl sulfoxide (DMSO) in refluxing acetic acid is an efficient trapping agent for thiols, oxidizing them to disulfides. When **1** or α-(phenylsulfinyl)acetic acid (**11**) is refluxed in acetic acid with DMSO, disulfide and aldehyde are formed. The behavior of α-(benzylthio)-*p*-nitrobenzyl alcohol (**10**) with DMSO in acetic acid is equivocal. The products are **4** and either **2** or disulfide, depending on the reaction conditions. The existence of an equilibrium between thiol and aldehyde on the one hand and monothiohemiacetal on the other is demonstrated. The behavior of **10** is readily interpreted in terms of this equilibrium. Mechanistic consequences of these results are discussed and it is concluded that it is unrealistic to talk of a single mechanism for these redox reactions of sulfoxides.

Sulfoxides react under a variety of acidic conditions with reduction at sulfur, oxidation at the α carbon, and, frequently, carbon–sulfur bond fission.[3] Prototype reactions were those of Pummerer,[4] as given in eq 1–3. It was suggested[5] that the reaction between



sulfoxide and carboxylic anhydride to form the ester of the corresponding monothiohemiacetal (eq 3) be designated "the Pummerer reaction." This fitting suggestion has received considerable acceptance.[6] Unfortunately, the term "Pummerer reaction" has been extended[7–9] to other redox reactions of sulfoxides. Implicit in these extensions appears to be the assumption that a single mechanism is applicable, regardless of the nature of the acidic medium and the structural features of the sulfoxide. In the absence of supporting experimental evidence, this assumption is gratuitous. The results reported here suggest that it is also erroneous.

(1) (a) Presented in part at the 16th Southeastern Regional Meeting of the American Chemical Society, Charleston, W. Va., Oct 1964, and in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 1968, Abstracts, p7P; (b) taken in part from the Ph.D. Thesis of J. A. W., Purdue University, June 1963, and in part from the M.S. Theses of D. B. M. and J. E. R., John Carroll University, Aug 1966 and May 1968, respectively.

(2) To whom all inquiries should be addressed.

(3) For a summary, see W. J. Kenney, J. A. Walsh, and D. A. Davenport, *J. Amer. Chem. Soc.*, **83**, 4019 (1961).

(4) (a) R. Pummerer, *Ber.*, **42**, 2282 (1909); (b) *ibid.*, **43**, 1401 (1910).

(5) L. Hörner, *Ann.*, **631**, 198 (1960).

(6) See, for example, S. Oae, T. Kitao, S. Kawamura, and Y. Kitaoka, *Tetrahedron*, **19**, 817 (1963), and C. R. Johnson, J. C. Sharp, and W. G. Phillips, *Tetrahedron Lett.*, 5299 (1967).

(7) H.-D. Becker, *J. Org. Chem.*, **29**, 1358 (1964).

(8) G. A. Russell and G. J. Mikol, *J. Amer. Chem. Soc.*, **88**, 5498 (1966).

(9) T. L. Moore, *J. Org. Chem.*, **32**, 2786 (1967).

Experimental Section[10]

Routine Preparations.—The following compounds were prepared by previously reported procedures and only recrystallization solvent, yield, physical constants, and/or microanalysis are given: α-(benzylthio)-*p*-nitrotoluene, 86%, mp 57–58° (lit.[11] mp 56–57°); benzyl sulfide, chloroform, 72% mp 49–50° (lit.[12] mp 49°); phenyl benzyl sulfide, ethanol, 98%, mp 41–43° (lit.[4b] mp 42°); α-(benzylsulfinyl)-*p*-nitrotoluene (**1**), benzene, 81%, mp 158.5–159° (lit.[13] mp 161–162°); benzyl sulfoxide **6**, aqueous ethanol, 69%, mp 133–134° (lit.[14] mp 134°); phenyl benzyl sulfoxide **8**, ethanol, 75%, mp 124–125° (lit.[4b] mp 125.5°); *p*-nitrobenzyl sulfone, 74%, mp 254–255° (lit.[15] mp 260°); α,α-di(benzylsulfonyl)-*p*-nitrotoluene, acetic acid,[16] 56%, mp 249–250° (lit.[17] mp 244°), with ir (Nujol) 1525, 1357, 1345, 1332, 1157, 701 cm^{-1} (*Anal.* Calcd for $C_{21}H_{19}NO_6S_2$: C, 56.60; H, 4.30; S, 14.40. Found: C, 56.60; H, 4.52; S, 14.51.); α,α-di(*p*-nitrobenzylsulfonyl)toluene, acetic acid,[16] 53%, mp 235.5–236°, with ir (Nujol) 1520, 1360–1305, 1160, 1140–1125, 858, 792, 696 cm^{-1} (*Anal.* Calcd for $C_{21}H_{18}N_2O_8S_2$: C, 51.41; H, 3.70; N, 5.71; S, 13.08. Found: C, 51.08; H, 3.86; N, 5.54; S, 13.48.).

Preparation of α,α-Di(benzylthio)-*p*-nitrotoluene (2).—A solution of 0.65 g (4.3 mmol) of *p*-nitrobenzaldehyde **4** and 1.09 g (8.5 mmol) of α-toluenethiol in 25 ml of acetic acid was refluxed for 10 hr and then poured onto ice. This mixture was extracted with ether and the ethereal layer was washed with water and dried (Na_2SO_4). Evaporation of the ether left a syrup which, when triturated with ethanol, deposited **2**. Recrystallization (acetic acid) gave **2** (71%): mp 79–80° (lit.[17] mp 72–74°); ir (CCl_4) 1599, 1520, 1490, 1450, 1343, 856, 698–696 cm^{-1}.

(10) All melting points, unless otherwise noted, were taken in open capillaries and are uncorrected. All yields are of pure materials. Microanalyses were by Dr. C. S. Yeh and Mrs. V. Keblys of Purdue. Most infrared absorption spectra were recorded on a Perkin-Elmer Model 21 or 221 spectrophotometer by Mrs. W. Dilling at Purdue. A few of the more recent ones (spectra marked *) were recorded on a Beckman IR-5A. Nmr spectra were recorded with a Varian A-60D spectrometer, using tetramethylsilane as an internal reference. When the term hydrogen peroxide is used, it should be taken to mean 30% by weight aqueous hydrogen peroxide, and acetic acid to mean redistilled glacial acetic acid.

(11) C. G. Overberger, S. P. Ligthelm, and E. A. Swire, *J. Amer. Chem. Soc.*, **72**, 2856 (1950).

(12) C. Marker, *Ann.*, **136**, 89 (1865).

(13) G. Leandri, A. Mangini, and R. Passerini, *J. Chem. Soc.*, 1386 (1957).

(14) M. Gazdar and S. Smiles, *ibid.*, 1835 (1908).

(15) W. R. Waldron and E. E. Reid, *J. Amer. Chem. Soc.*, **45**, 2411 (1923).

(16) Compounds in this *p*-nitrobenzyl series have been found to cling rather tenaciously to residual acetic acid. Where recrystallization from this solvent is required, this strongly held acetic acid can be removed by prolonged, vigorous stirring of the sample as a suspension in water or better, if possible, in alcohol.

(17) T. Posner, *Ber.*, **35**, 2348 (1902).

Anal. Calcd for $C_{21}H_{19}NO_2S_2$: C, 66.10; H, 5.02. Found: C, 66.38; H, 5.31. Preparation of the disulfone confirmed the structure.

Preparation of α,α-Di(*p*-nitrobenzylthio)toluene (3).—A solution of 12.60 g (0.058 mol) of *p*-nitrobenzyl bromide and 31.15 g (0.32 mol, if anhydrous) of potassium thiocyanate in 100 ml of absolute ethanol was refluxed for 12 hr. After the solvent had been stripped and the inorganic salts had been removed with water, the yellow *p*-nitrobenzyl thiocyanate remained. Recrystallization (aqueous ethanol) gave 8.36 g (73.8%) of product, mp 83.5–84.0° (lit.[18] mp 85.5°).

Conversion of thiocyanate into thiocarbamate was carried out in a 32°F cold room. Addition of 8.36 g (0.043 mol) of *p*-nitrobenzyl thiocyanate to 44.5 ml of concentrated sulfuric acid produced immediate homogeneity. After the reaction mixture had stood for 12.5 hr, the product was precipitated by pouring the mixture onto ice. Recrystallization (*n*-amyl alcohol) gave very pale yellow *p*-nitrobenzyl thiocarbamate (94%), mp 142–144° (lit.[19] mp 146°).

Reflux of 8.62 g (0.04 mol) of the thiocarbamate in 80 ml of 20% aqueous hydrochloric acid for 1.5 hr formed a dense, immiscible oil. Cooling crystallized the oil to a tan cake. Extraction with two 20-ml portions of acetic acid dissolved most of the cake to give a pale yellow solution of *p*-nitrobenzylthiol.[20]

The acetic acid insoluble material was recrystallized (acetic acid) to give *p*-nitrobenzyl sulfide (43%), mp 157–159° (lit.[23] mp 159°). The identification was confirmed by oxidizing the sulfide to the sulfone.

To the acetic acid solution of *p*-nitrobenzylthiol was added a solution of 2.15 g (0.02 mol) of benzaldehyde in 5 ml of acetic acid. In 5 min crystallization began. After standing for 2 hr, the precipitate was filtered, washed with water, and vacuum dried to give 3.79 g (76.6%) of **3**, mp 138–140°. Two recrystallizations (acetic acid) gave mp 142–143°; ir ($CHCl_3$) 1610, 1525, 1350, 1110, 859 cm^{-1}.

Anal. Calcd for $C_{21}H_{18}N_2O_4S_2$: C, 59.13; H, 4.25; N, 6.57; S, 15.04. Found: C, 59.03; H, 4.19; N, 6.33; S, 15.33.

3 was found to be very soluble in chloroform, soluble to the extent of 0.23 g/100 ml in boiling absolute ethanol, and insoluble in carbon tetrachloride.

The identity of **3** was confirmed by converting it into α,α-di(*p*-nitrobenzylsulfonyl)toluene.

Reaction of 1 in Acetic Acid.—A solution of 2.62 g (9.5 mmol) of **1** in 15 ml of acetic acid was refluxed for 24 hr. The reaction mixture was quenched in 135 g of ice–water. The resulting milky suspension was filtered through a Soxhlet thimble. The residue in the thimble was continuously extracted by this filtrate for 50 hr. On cooling, a hairy, white solid precipitated. It was filtered and dried to give 0.58 g of *p*-nitrobenzaldehyde **4**: mp 101–103° (lit.[24] mp 106°); ir (saturated $CHCl_3$ solution) 2790, 1705, 1600, 1520, 1380, 1342, 1318, 1290, 1188, 846 cm^{-1}. The phenylhydrazone recrystallized (aqueous ethanol) as a deep red powder, mp 154–155° dec (lit.[25] mp 155°).

The aqueous filtrate was neutralized with 1.5 *M* sodium carbonate solution and concentrated to near dryness. This small residue was picked up in 20 ml of absolute ethanol and treated with a solution of 0.24 g of 2,4-dinitrophenylhydrazine and 6 ml of 12 *M* hydrochloric acid in 10 ml of absolute ethanol, forming 0.25 g of the 2,4-dinitrophenylhydrazone of **4**, mp 320° (lit.[26] mp 320°). The ir (Nujol) of this derivative was in detailed agreement with that of an authentic sample. Based on reaction to thioacetal and aldehyde, 97.2% of **4** was accounted for.

The residue from the thimble was crushed to a tan powder, mp 64–68°. The thimble itself was extracted first with ether and then with boiling absolute alcohol. The residue from the evaporation of these combined extracts was added to the tan powder and the whole was recrystallized from 20 ml of absolute ethanol, giving 1.01 g of **2**, mp 74–76°. The ir was in detailed agreement with that of an authentic sample. Concentration of the mother liquor and dilution with water produced another 0.21 g of **2**, mp 72–78°. The residual filtrate was dissolved in 20 ml of acetic acid and refluxed for 16 hr with 7.01 g (61.8 mmol) of hydrogen peroxide. Then, pouring the reaction mixture onto ice, filtering, and drying gave 0.16 g of α,α-di(benzylsulfonyl)-*p*-nitrotoluene, ir (Nujol) in detailed agreement with that of an authentic sample. This brought to 73% the **2** accounted for and represented on over-all material balance of 86%. An infrared study of 2,4-dinitrophenylhydrazones from duplicate aliquots of crude reaction mixture indicated that the carbonyl portion of the product was better than 99% **4**.

Reaction of 1 in Ether with Hydrogen Chloride.—A suspension of 3.65 g (13.3 mmol) of **1** in 200 ml of dry ether was treated with a steady stream of dry hydrogen chloride in the cold until all **1** had dissolved. After this clear solution had stood at room temperature for 22 hr, 106 ml of solvent were distilled. The residual solution was washed with water until the washings were neutral and then it was extracted with several portions of dilute sodium hydroxide solution. Neutralization of the combined extracts, followed by ether extraction, provided only a negligible amount of benzyl disulfide.

The remaining ethereal solution, on standing, deposited 0.1 g of white, crystalline solid, mp 138–139°. The ir ($CHCl_3$) proved to be identical in every detail with that of **3**.

Evaporation of the ether filtrate gave 2.94 g of lemon-yellow solid. Fractional crystallization (aqueous ethanol) gave 1.0 g of pure **2** plus mixtures of **2** and **3**.

Isotope Dilution Analysis. β-Particle Counting Equipment.—A thin-window Geiger–Muller (G–M) tube from Atomic Accessories, Inc., was used. The tube model was EWT-64, with an operating voltage of 1300 and window thickness of 1.4 mg/cm². The tube was used with a Picker, Model 2951, single-channel scaler. The G–M tube was mounted in a hollowed lead bar of 2-cm wall thickness. The lead cylinder and G–M tube were placed directly over the sample-containing planchet, ensuring that the sample was a constant distance from the tube for each counting period.

Values used for the sample and background count were the average of at least three 10-min counting periods. Background count was determined each day that data were taken.

The time interval between adding active dithioacetal and counting recovered mixture was always nearly 48 hr. Decrease in activity of radioactive dithioacetal for this time interval was calculated according to the first-order rate law. Dead-time value for the G–M tube used was 0.5%/1000 counts/min.[27] The dead-time corrections for the slow count rates were negligible. Samples of the pure, active dithioacetals added and resulting mixtures obtained were by design always very nearly the same weight so that self-absorption effects were approximately constant.

Preparation of Sulfur-35-Labeled Compounds.—Sulfur-35 (50 μCi) (Nuclear Chicago Corp.) as elemental sulfur in toluene were mixed with 0.2 g of sulfur-32 to give sulfur enriched in sulfur-35.

In preparation of radio-tagged **3**, the sulfur-35 was first converted into potassium thiocyanate by the standard method[28] and then as described for inactive sulfur. From 50 mg (1.5 mmol) of enriched sulfur, with no purification of intermediate products, was obtained 37.4 mg (11.7%) of **3**, enriched in sulfur-35, mp 138–140°.

In the preparation of radio-tagged **2**, the sulfur-35 was first converted into α-toluenethiol by the method of Wood, *et al.*,[29] and then the procedure was as that described for inactive sulfur. From 50 mg (1.5 mmol) of enriched sulfur, with no purification of intermediate products, 10.4 mg (3.5%) of **2**, enriched in sulfur-35, mp 78–79.5°, was obtained.

Reaction of α-(Benzylsulfinyl)-*p*-nitrotoluene (1) with Hydrogen Chloride and Quantitative Determination of Products by Isotope Dilution Analysis.—A suspension of 3.0610 g (11.1 mmol) of **1** in 200 ml of dry ether was prepared. While the suspension was kept cold and constantly stirred, dry hydrogen chloride gas was bubbled in until all **1** had dissolved. The re-

(18) J. A. Lyman and E. E. Reid, *J. Amer. Chem. Soc.*, **39**, 702 (1917).

(19) G. M. Bennet and W. A. Berry, *J. Chem. Soc.*, 1666 (1927).

(20) As others,[19] we found the method of Price and Twiss[21] unsatisfactory. The only products which we could isolate and characterize were *p*-nitrobenzyl disulfide, mp 122–124° (lit.[21] mp 126°), and *p*-nitrobenzyl alcohol, mp 94–95° (lit.[22] mp 93°).

(21) T. S. Price and D. F. Twiss, *ibid.*, 1727 (1909).

(22) F. Beilstein and A. Kuhlberg, *Ann.*, **147**, 343 (1868).

(23) O. Fischer, *Ber.*, **28**, 1338 (1895).

(24) O. Fischer, *ibid.*, **14**, 2525 (1881).

(25) M. Pickel, *Ann.*, **232**, 232 (1886).

(26) O. L. Brady, *J. Chem. Soc.*, 756 (1931).

(27) Value provided by Dr. Lawrence Becker, Department of Physics, Hiram College. We wish to thank Professor Becker for the use of the counting equipment and for his interest and assistance.

(28) J. L. Wood, E. F. Williams, Jr., and N. Kingsland, *J. Biol. Chem.*, **170**, 251 (1947).

(29) J. L. Wood, J. R. Rachele, C. M. Stevens, F. H. Carpenter, and V. duVigneaud, *J. Amer. Chem. Soc.*, **70**, 2547 (1948).

action mixture was then divided into two equal portions, designated A and B.

To portion A was added 9.52 mg of α,α-di(*p*-nitrobenzylthio)-toluene-^{35}S, average activity for five counting periods 118,680 counts/10 min (average background count for five counting periods 534 counts/10 min). The mixture was allowed to stand for 21 hr and then the volume was reduced to about 50 ml on a water bath. The ether solution was washed with water until neutral to litmus. On standing 2 hr, this ethereal solution precipitated **3**, which on recrystallization (acetic acid) had mp 138–140°. After recrystallization, the sample was stirred vigorously with ethanol for several hours and then filtered, dried, weighed, and counted. A 10.04-mg sample of this **3** had an average activity for three counting periods of 2306 counts/10 min (average background count for three counting periods, 527 counts/10 min). Calculation[30] showed that 1.37 g (3.22 mmol, 57.9%) of **3** was present in the reaction mixture.

To portion B was added 10.42 mg of α,α-di(benzylthio)-*p*-nitrotoluene-^{35}S, average activity for three counting periods 77,705 counts/10 min. The mixture was treated exactly as portion A to obtain 50 ml of neutral, ethereal solution and **3**, mp 138–140°. The **3** was removed and the clear filtrate was evaporated to dryness. The residue was dissolved in absolute ethanol and allowed to stand. In 4 hr crude crystals of **2** had formed. Recrystallization (acetic acid) gave pure **2**, mp 78–79°. Again, stirring with alcohol preceded weighing and counting of the dry sample. A 11.75-mg sample of this **2** had an average activity for three counting periods of 2587 counts/10 min (average background count for three counting periods, 513 counts/10 min). Calculation[20] showed that 0.89 g (2.34 mmol, 42.1%) of **2** was also present in the reaction mixture.

A duplicate run with an identical sample of sulfoxide showed 1.25 mg (2.95 mmol, 53.1%) of **3** and 1.00 mg (2.62 mmol, 47.2%) of **2** in the product mixture.

Reactions of 6. 1.—A solution of 1.24 g (5.38 mmol) of **6** in 75 ml of acetic acid was refluxed for 20 hr. After distillation had reduced the pot residue to 10 ml, quenching with water precipitated a white solid, which smelled of thiol. Recrystallization (aqueous ethanol) gave 1.0 g of material, mp 118–122°. The ir (Nujol) indicated this to be primarily recovered **6** with traces of unidentified contaminant.

2.—A suspension of 3.25 g (14.1 mmol) of **6** in 50 ml of 6 *M* sulfuric acid was diluted with 50 ml of acetic acid. When warmed on a steam cone the mixture became homogeneous. After 10 days of heating, a small pool of immiscible liquid had formed. When the reaction mixture was poured in ice–water, 1.56 g of a fluffy white solid, mp 114–121°, was obtained. An ir spectrum (Nujol) disclosed it to be primarily recovered **6** with trace contamination.

3.—To a solution of 2.3 g (10 mmol) of **6** in 75 ml of acetic acid, 1.0 ml of 1.0 *N* sulfuric acid was added. After refluxing for 4 months and quenching on ice, a tan solid precipitated. Recrystallization (absolute ethanol) gave a quantitative yield of benzyl disulfide **7**, mp 65–67° (lit.[31] mp 71–72°). The ir of this material was in detailed agreement with that of an authentic sample.

Attempted Reaction of 8.—A solution of 2.16 g (10 mmol) of **8** in 25 ml of acetic acid was refluxed for 20 hr. Cooling, quenching in ice–water, filtering, and drying gave a recovery of **8** (97%), mp 124–125°.

Preparation of Ethyl α-(*p*-Nitrophenylsulfinyl)acetate.—*p*-Nitrobenzenethiol was prepared (75%) by the method of Prince and Stacy.[32] A mixture of 14.5 g (0.09 mol) of thiol, 12.26 g (0.1 mol) of ethyl chloroacetate, and 7.91 g (0.1 mol) of pyridine in 350 ml of dry ether was refluxed for 17 hr. Filtration removed the brick-red ether-insoluble disulfide, and evaporation left a pale yellow solid. Washing with water and drying gave 19.0 g (84%) of ethyl α-(*p*-nitrophenylthio)acetate. Recrystallization (ligroin) gave mp 44.5–48° (lit.[33] mp 46–47°).

A solution of 10.43 g (43 mmol) of sulfide and 4.90 g (43 mmol) of hydrogen peroxide in 160 ml of acetic acid was kept at room temperature for 4.5 days.[34] Quenching in ice–water gave a beige precipitate which, when dry, amounted to 8.03 g (72%) of the sulfoxide, mp 74–82°. Several recrystallizations (aqueous ethanol) gave an off-white powder which, because of static electricity, was difficult to manipulate and had mp 94.5–95.5°; ir [$CHCl_3$] 1740, 1530, 1370, 1345, 1285 (broad), 1085, 1055, 853 cm^{-1}.

Anal. Calcd for $C_{10}H_{11}NO_5S$: C, 46.69; H, 4.31; S, 12.47. Found: C, 46.68; H, 4.40; S, 12.77.

Reaction of Ethyl α-(*p*-Nitrophenylsulfinyl)acetate.—A solution of 1.89 g (7.35 mmol) of the sulfoxide in 50 ml of trifluoroacetic acid was refluxed for 12 hr.[35] Quenching in ice–water gave 1.30 g (89.7%) of ethyl α,α-di(*p*-nitrophenylthio)acetate which, after two recrystallizations (acetic acid), had mp 120–121°; ir ($CHCl_3$): 1745, 1590, 1523, 1350, 1285, 855 cm^{-1}.

Anal. Calcd for $C_{16}H_{14}N_2O_6S_2$: C, 48.72; H, 3.58; N, 7.10; S, 16.26. Found: C, 48.53; H, 3.83; N, 6.82; S, 16.16.

Ethyl glyoxylate in the aqueous filtrate was identified as its phenylhydrazone, mp 134° (lit.[36] mp 131°).

Preparation of α,α-Di(*p*-nitrophenylthio)acetic Acid.—A solution of 2.03 g (8.78 mmol) of α-(*p*-nitrophenylsulfinyl)acetic acid[3] in 50 ml of trifluoroacetic acid was refluxed for 19.5 hr. The wine-red mixture was quenched on ice to give 1.50 g (92.7%) α,α-di(*p*-nitrophenylthio)acetic acid. Two recrystallizations (acetic acid) gave a dark yellow powder: mp 183.5–184.5°; ir (Nujol) 1720, 1520, 1345, 857, 742 cm^{-1}.

Anal. Calcd for $C_{14}H_{10}N_2O_6S_2$: C, 45.88; H, 2.75; N, 7.65; S, 17.51. Found: C, 45.83; H, 2.85; N, 7.42; S, 17.46.

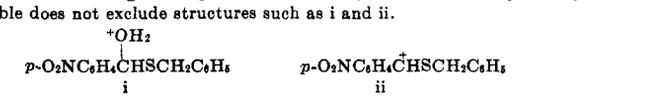
From the aqueous filtrate 1.04 g (93.2%) of the 2,4-dinitrophenylhydrazone of glyoxylic acid, mp 188–190° dec (lit.[26] mp 190° dec), was isolated.

Preparation of α-(Benzylthio)-*p*-nitrobenzyl Alcohol (10).—To 250 ml of anhydrous ether was added 7.55 g (50 mmol) of **4**. After all of the solid had dissolved, 6.20 g (50 mmol) of α-toluenethiol was added all at once.[37] After 18 hr, the ether was removed *in vacuo* to give **10** (92%): mp 50–51° (sealed tube); ir* (KBr) 3325, 1498, 1308, 1025, 690 cm^{-1}. The structure of **10** was confirmed as follows. (1) Reflux of a mixture of 25 ml of acetic acid and 1.40 g (5 mmol) **10**, quenching in ice–water, and recrystallization (methanol) gave 0.85 g (89%) of **2**, mp 79–80°, mixture melting point with authentic sample undepressed. **4** was identified (90%) as the phenylhydrazone. (2) To 25 ml of acetic acid were added 0.62 g (5 mmol) α-toluenethiol and 1.40 g (5 mmol) of **10**. After this solution had stood at room temperature for 16 hr, it was refluxed for 1 hr. Quenching in ice–water and recrystallization (methanol) gave 1.63 g (86%) **2**, mp 78.5–80°, mixture melting point with authentic sample undepressed.

The nmr spectrum of **10** was run at room temperature in a variety of solvents. In CCl_4 the following data were obtained: δ 1.56 (t, 1, J = 7 Hz, –SH), 3.74 (d, 2, J = 7 Hz, $ArCH_2S$–), 7.30 (s, 5, C_6H_5–), 8.06, 8.36 (d, d, 4, J = 9 Hz, *p*-$O_2NC_6H_4$–), 10.18 (s, 1, –CHO). In acetic acid-d_4 the following data were obtained (peak areas are given in relative units): δ 3.69 (s, 16), 3.83, 3.99 (d, d, 22), 6.00 (s, 11), 7.32 (s, 99), 7.66 (d, 24), 8.05–8.36 (m, 57), 10.16 (s, 8), 11.50 (broadened s, 19). This spectrum was clearly that of a mixture interpreted as follows: δ 3.69 (s, 2, $C_6H_5CH_2SH$), 3.83, 3.99 (d, d, 2, J = 12 Hz, $-CH_2-$ in **10**[38]), 6.00 (s, 1, >CH– in **10**), 7.32 (s, 5, both $C_6H_5CH_2SH$ and $C_6H_5CH_2S$– in **10**), 7.66, 8.14 (d, d, 4, J = 9 Hz, *p*-$O_2NC_6H_4$– in **10**), 8.05, 8.36 (d, d, 4, J = 9 Hz, *p*-$O_2NC_6H_4$-CHO), 10.16 (s, 1, –CHO), 11.50 (broadened s, 1, –OH and –SH). An equilibrium in which 40% of **10** has dissociated to α-toluenethiol and **4** is in good agreement with these data. An identical spectrum was also obtained by mixing α-toluenethiol and **4** (1:1) in acetic acid-d_4 at room temperature.

Trapping Experiments.—Unless otherwise stated, all of these reactions were conducted in 150 ml of acetic acid, with 20 mmol of each reactant, at reflux for 20 hr. Work-up was by quenching the reaction mixture in 10 times its volume of ice–water and filtering. The identity of all sulfur-containing products was

(30) K. Block and H. S. Anker, *Science*, **107**, 228 (1948).
(31) O. Hinsberg, *Ber.*, **41**, 632 (1908).
(32) C. C. Price and G. W. Stacey, *J. Amer. Chem. Soc.*, **68**, 498 (1946).
(33) P. Friedlander and A. Chwala, *Monatsh. Chem.*, **28**, 275 (1907).
(34) Shorter reaction times gave considerable unreacted sulfide; heating led to small yields of the disulfide and intractable emulsions.
(35) Refluxing for 67 hr in acetic acid led to a 43% recovery of the sulfoxide and an intractable emulsion.
(36) W. Oroshnik and P. E. Spoerri, *J. Amer. Chem. Soc.*, **63**, 3338 (1941).
(37) For some reason, presently unknown, the sequence of addition is important, and inverse addition gave mixtures from which **10** could be isolated only with difficulty.
(38) While we assign this species structure **10**, the information presently available does not exclude structures such as i and ii.



i ii

confirmed by mixture melting point with authentic samples. No depressions were observed. Yields of aldehyde, where quoted, were obtained in part by isolation and, in part, by preparation of the phenylhydrazone.

1 and DMSO were dissolved at room temperature and refluxed. One product, after recrystallization (methanol), was **7** (87%), mp 69–71°. The other was **4** (92%).

α-Toluenethiol and DMSO under identical conditions gave **7** (90%).

A solution of 20 mmol of DMSO in 50 ml of acetic acid was refluxed. To this, two solutions were added simultaneously, dropwise, over a 2-hr period. One of these solutions had 20 mmol of α-toluenethiol in 50 ml of acetic acid: the other, 20 mmol of **4** in 50 ml of acetic acid. The products were **7** (88%), mp 69–70°, and recovered **4**.

In a separate experiment, **4** was recovered unchanged after 20 hr of reflux in acetic acid containing an equivalent amount of DMSO. However, it was observed that DMSO, itself, slowly decomposed into thus far unidentified products under these conditions.

α-Toluenethiol and **4** were dissolved and allowed to stand at room temperature for 12 hr. Then DMSO was added and the solution was refluxed. One product, after recrystallization (methanol), was **2** (98%), mp 78.5–80°. The other was **4** (93%).

10 and DMSO were dissolved at room temperature and the solution was brought to reflux (about 45 min). The products were **2** (97%) and **4** (92%).

A solution of 0.78 g (10 mmol) of DMSO in 75 ml of acetic acid was refluxed. To this were added in small portions over a 2-hr period 2.79 g (10 mmol) of **10**. Fractional crystallization (methanol) of the product mixture gave 0.18 g (14%) of **2**, mp 79–81°, and 1.02 g (81%) of **7**, mp 69–70°.

A solution of 0.78 g (10 mmol) of DMSO in 37.5 ml of acetic acid was refluxed. To this was added dropwise, over a 4-hr period, a solution of 2.79 g (10 mmol) of **10** in 37.5 ml of acetic acid. The product, after recrystallization (methanol), was 1.11 g (90%) of **7**, mp 69–71°.

A "supersaturated aqueous solution" of **11** was prepared[39] by mixing 11.4 ml of hydrogen peroxide and 16.8 g (100 mmol) of α-(phenylthio)acetic acid[3] and stirring at 0° until homogeneous. To this, 7.8 g (100 mmol) of DMSO was added and the mixture was refluxed for 20 hr. The solid obtained on cooling gave, after recrystallization (aqueous methanol), 9.4 g (87%) of phenyl disulfide, mp 57–59° (lit.[40] mp 61.5°).

A solution of 1.84 g (10 mmol) of **11** and 0.78 g (10 mmol) of DMSO in 75 ml of acetic acid was refluxed for 18 hr. The product, after recrystallization (methanol), was 0.81 g (74%) of phenyl disulfide, mp 57–58°.

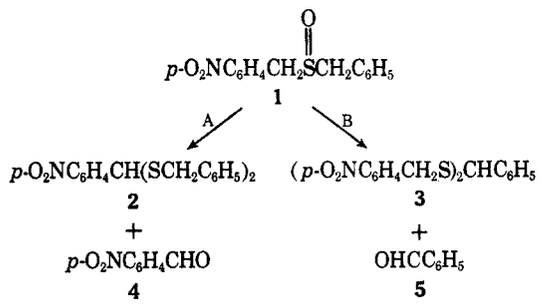
Results and Discussion

A. The Reaction in Acetic Acid.—Much of our previous work involved reaction in refluxing glacial acetic acid of sulfoxides activated by an electron-withdrawing group (Y) on the α carbon (eq 4). To

$$2R\overset{\overset{O}{\|}}{S}CH_2Y \xrightarrow[\Delta]{[HOAc]} [RS]_2CHY + OHCY + H_2O \quad (4)$$

probe the details of this reaction, the behavior of α-(benzylsulfinyl)-*p*-nitrotoluene (**1**) was examined. As shown in Chart I, intramolecular competition is possible. Path A, with *p*-nitrobenzyl–sulfur bond fission, would produce α,α-di(benzylthio)-*p*-nitrotoluene (**2**) and *p*-nitrobenzaldehyde (**4**). Path B would give α,α-di(*p*-nitrobenzylthio)toluene (**3**) and benzaldehyde **5**. While they are by no means the only conceivable products, dithioacetal and aldehyde are usual ones from this redox reaction of activated sulfoxides. When **1** was refluxed in acetic acid for 24 hr, the products isolated were exclusively **2** and **4**, *i.e.*, path A. Dithioacetal **3** was synthesized and its characteristics were found

CHART I



to be sufficiently different from those of **2** that even small quantities of **3** would have been detected had they been present. Infrared examination of 2,4-dinitrophenylhydrazones failed to show **5** in the reaction mixture, though an independent control indicated that as little as 1 mol % could be detected.

In contrast, reflux of benzyl sulfoxide **6** in acetic acid for 20 hr gave 80% recovery of sulfoxide. Much longer reflux times with sulfuric acid catalysis led to complete conversion into benzyl disulfide **7**. When α-(phenylsulfinyl)toluene (**8**) was refluxed in acetic acid for 20 hr, 97% of it was recovered unchanged. Similarly, dimethyl sulfoxide showed only slow decomposition under these conditions.

Thus, *for facile reaction in refluxing glacial acetic acid, the presence on the α carbon of an electron-withdrawing, activating group is essential.*

The nature of the slow reaction of unactivated sulfoxides needs further study. Thermal decomposition of sulfoxides was reported[41] early and has recently attracted renewed attention.[42,43] It would be useful to know if this slow reaction is facilitated by acid.

Originally we speculated[3] that reaction of activated sulfoxides in acetic acid proceeds by S protonation, rearrangement to a protonated sulfenate, and cleavage to thiol and aldehyde, regenerating the catalytic proton. Thiol and aldehyde recombined to form monothiohemiacetal which protonates and ionizes to a sulfonium–carbonium hybrid ion. This ion then adds thiol and loses a proton to give dithioacetal.

Although a sulfoxide → sulfenate rearrangement has been invoked[42] to explain the decomposition of benzylic sulfoxides to benzaldehydes at 220°, rearrangement of S-protonated sulfoxide to protonated sulfenate remains unconfirmed. Recently, there have been reports of a reverse reaction, sulfenate → sulfoxide.[44–46] The principle of microscopic reversiblility requires that rearrangement of sulfoxides to sulfenates be possible. We are simply suggesting that, for activated sulfoxides, acetic acid may provide an energetically favorable reaction path for this rearrangement.

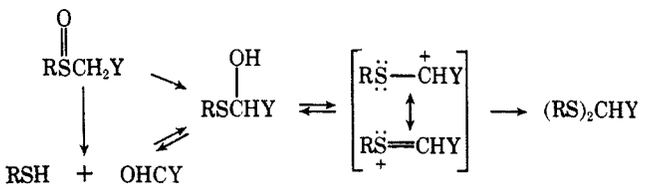
Walker and Leib[39] took exception to our speculative mechanism. They too studied α-(phenylsulfinyl)acetic acid (**11**) but in aqueous solution, with no acid other than substrate. In the product mixture they reported monothiohemiacetal, dithioacetal, phenyl disulfide, and

(39) D. Walker and J. Leib, *Can. J. Chem.*, **40**, 1242 (1962).
(40) W. Steinkopf, I. Schubart, and S. Schmidt, *Ber.*, **61**, 680 (1928).
(41) E. Fromm and O. Achert, *ibid.*, **36**, 534 (1903).
(42) W. Carruthers, I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *Chem. Ind.* (London), 342 (1966).
(43) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, **88**, 3138 (1966).
(44) E. G. Miller, D. R. Rayner, and K. Mislow, *ibid.*, **88**, 3139 (1966).
(45) S. Braverman and Y. Stabinsky, *Chem. Commun.*, 270 (1967).
(46) D. J. Abbott and C. J. M. Stirling, *ibid.*, 165 (1968).

unreacted **11** in amounts varying with reaction conditions. Their mechanistic conclusions lean heavily on results of their scavenger experiments. These were run with concentrated sulfuric acid in aqueous acetic acid, reaction conditions substantially different not only from ours but also from their own product studies. Since the course of the reaction is sensitive to the reaction conditions, this complicates the issue. Hydrazine sulfate was used as scavanger for glyoxylic acid but nowhere in the details of these experiments was there mention of the isolation of *any* of the expected derivative of glyoxylic acid. Again, the material balances were disturbing. Benzenethiol and **11** gave 32% α,α-di(phenylthio)acetic acid in the presence of the hydrazine and 40% in its absence. Benzenethiol and glyoxylic acid gave 14.5% of the dithioacetal in the absence of the hydrazine and none in its presence. No other products were mentioned and, in the latter experiment, no product of any description was reported. Thus, in all of these scavenger experiments, the fate of the vast majority of the starting material was unreported. This is unfortunate and cannot help but compromise arguments based on these results.

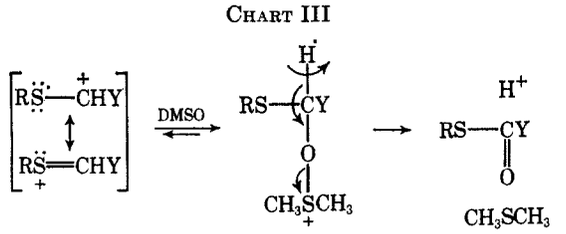
The interpretation of Walker and Leib is that monothiochemiacetal forms by intramolecular rearrangement of O-protonated sulfoxide. The crux of their disagreement with our original speculation is this: prior to formation of monothiohemiacetal, has there been carbon–sulfur bond fission? The situation is summarized in general terms in Chart II.

Chart II



Our dissatisfaction with these scavenger experiments prompted us to search for a more efficient trapping system. The sulfonium–carbonium hybrid ion had been implicated[47] as a likely intermediate in the formation of dithioacetal from thiol and aldehyde. In view of the report[7] of the conversion of 2-methylsulfinyl-1,3-indandione into 2-ethoxy-2-methylthio-1,3-indandione in ethanol, it appeared that this hybrid ion might be especially vulnerable to trapping by nucleophiles. The nucleophilicity of DMSO is well known and we thought that it might trap the hybrid ion and produce thiol ester and dimethyl sulfide (Chart III).

Chart III



Reflux of **1** in acetic acid containing an equimolar quantity of DMSO evolved dimethyl sulfide. However, work-up of the remaining solution gave no thiol ester but rather **7** (87%) and **4** (92%). Apparently, DMSO oxidized intermediate thiol to disulfide. Similar oxidations had been reported,[48] but not in acetic acid. This explanation was supported by the fact that reaction of α-toluenethiol with DMSO under the same conditions also gave **7** (90%).

These results indicated that DMSO was an efficient trapping agent but for the thiol and *not* the hybrid ion. To test the plausibility of our mechanistic picture,[3] conditions were simulated for that stage of the reaction at which trapping would occur. Two solutions were added simultaneously, dropwise, over a 2-hr period to a refluxing solution of DMSO in acetic acid. One solution contained α-toluenethiol, the other, **4**, each in acetic acid. Reactants were in equimolar quantities. The products were **7** (88%) and **4**.

Therefore, examination of the behavior of α-(benzylthio)-*p*-nitrobenzyl alcohol (**10**) was essential. A solution of **10** (prepared *in situ*) in acetic acid was treated with 1 equiv of DMSO and refluxed. The products were **2** (98%) and **4** (93%). To avoid objections raised because of *in situ* preparation, **10** was prepared, isolated, and characterized (see Experimental Section). When a solution of equimolar amounts of DMSO and **10** in acetic acid was prepared at room temperature and then refluxed, **2** (97%) and **4** (92%) were obtained.

At this point, the fact that both the sulfoxide and the thiol–aldehyde mixture gave disulfide while the monothiohemiacetal gave dithioacetal strongly suggested that the thiol appeared *before* the monothiohemiacetal in the reaction sequence. However, **10** still had not been rigorously tested under conditions simulating those of the sulfoxide reaction. To do this, **10** was added slowly, in small amounts, to a refluxing solution of DMSO in acetic acid. Surprisingly, the product mixture contained mainly **7** (81%) with **4** and very little (14%) **2**. When an acetic acid solution of **10** was added slowly to a refluxing solution of DMSO in acetic acid, **7** (90%) was again formed. Thus, unexpectedly, the products obtained from **10** depend on the sequence of addition and reflux. Such results demonstrate the ease with which one may be misled in this system by trapping experiments which are less than thorough.

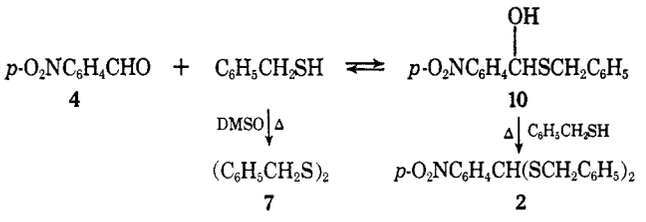
Partial explanation for this variation was obtained by studying the behavior of **10** in solution. Nmr spectra of solutions of **10** in CCl_4 and $CDCl_3$ run immediately after preparation revealed complete dissociation to thiol and aldehyde. In contrast, solutions of **10** in acetic acid-d_4 showed this dissociation to be only 40% complete. The undissociated portion may be present as **10**, or its conjugate acid or possibly the hybrid ion (see Experimental Section) but unequivocal identification requires more information. The nmr spectrum of a freshly prepared solution of α-toluenethiol and **4** in acetic acid-d_4 was identical with that obtained from **10**. There was no detectable change in the nmr spectrum of either solution after several days at room temperature. Our interpretation of these results is that thiol and aldehyde form monothiohemiacetal reversibly with equilibrium[49] being established rapidly in acetic acid

(47) E. Campaigne and J. R. Leal, *J. Amer. Chem. Soc.*, **76**, 1272 (1954).

(48) T. J. Wallace and J. J. Mahon, *Chem. Ind.* (London), 765 (1965), and references therein.

(49) The influence of structure and temperature on this equilibrium are being studied and will be reported separately.

CHART IV



at room temperature. Chart IV summarizes these interactions. Addition of **10** to acetic acid generates some thiol and **4** by reversible decomposition. Then, two major competing reactions are possible, (A) the conversion of **10** into **2** (rate, R_t) and (b) DMSO oxidation of thiol to **7** (rate, R_d). Our results would be most easily explained if, at reflux, $R_d > R_t$, while at some temperature between room and reflux, $R_t > R_d$.

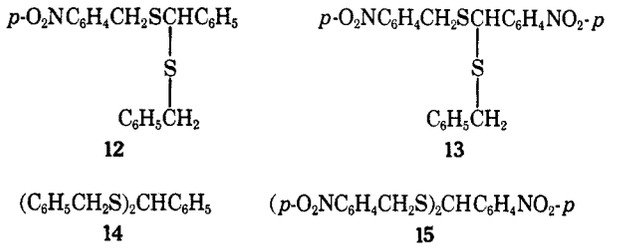
Since **1**, α-toluenethiol, and **10** all give **7** with DMSO in acetic acid under identical conditions, these results provide no information about the sequence in which thiol and monothiohemiacetal occur. In fact, the situation is further complicated because regardless of which forms first; it rapidly generates the other. For trapping experiments to specify the reaction sequence in this system what is necessary is a reagent and a well-defined, carefully controlled set of conditions with which thiol and monothiohemiacetal give *different* products. This requires that the trapping of both of these species be faster than their interconversion. These restrictions provide formidable obstacles to the design of truly meaningful trapping experiments.

Less extensive trapping experiments were conducted on α-(phenylsulfinyl)acetic acid. When the redox reaction of authentic **11** was run with DMSO, phenyl disulfide (74%) was obtained. Use of Walker and Leib's supersaturated aqueous solution" of **11** also gave disulfide (87%). Therefore, qualitatively, **1** and **11** behave similarly under identical conditions and it is likely that there exists for **11** a frustrating equilibrium similar to that found for **1**. Efforts to confirm this are in progress.

B. The Reaction in Trifluoroacetic Acid.—When α-(*p*-nitrophenylsulfinyl)acetic acid (**9**) was refluxed for prolonged periods in acetic acid or warmed for shorter periods in 6 *N* sulfuric acid, the sole sulfur-containing product was *p*-nitrophenyl disulfide.[3] However, when **9** was refluxed in trifluoroacetic acid, α,α-di(*p*-nitrophenylthio)acetic acid (93%) and glyoxylic acid were obtained. Similar treatment of ethyl α-(*p*-nitrophenylsulfinyl)acetate gave its dithioacetal (90%). These results provide further illustration that the course of redox of activated sulfoxides is sensitive to the reaction conditions.

C. The Reaction with Hydrogen Chloride.—Treatment of **1** with hydrogen chloride in dry ether at room temperature gave both **2** and **3** (paths A and B, Chart I). Sulfur-35 isotope dilution analysis showed that the reaction mixture contained 45 ± 3% **2** and 55 ± 3% **3**. Thus, reactivity at the two α carbons was roughly 1:1. We do not believe that any great significance should be read into the small deviation from 1:1, although it is beyond the limits of experimental error. However, it is curious that, under these conditions, the major product is the one which is unobserved in acetic acid. Thus the *p*-nitrophenyl group which was so influential in determining the products from **1** in acetic acid here appears passive.

For the reaction of activated sulfoxides in acetic acid, thiol and aldehyde—whether as products from, or precursors of, monothiohemiacetal—are likely intermediates. If they performed a similar function in the hydrogen chloride reaction, six dithioacetal products would be possible. One might fault the stability[50] of the mixed dithioacetals **12** and **13**, but symmetrical **14** and **15** cannot be discredited so easily. The experimental facts are clear: **2** and **4** are the dithioacetal products; they account, within experimental error, for all of the original sulfur; there is no sign of **14** and/or **15**. Perhaps thiol and aldehyde are not joint intermediates in the hydrogen chloride reaction.



Formation of **3** from **1** suggests that here the presence of an electron-withdrawing, activating group is no longer crucial. Therefore, unactivated sulfoxides should also be susceptible and the literature provides several instances. Thus, Smythe[51] found that **6** with hydrogen chloride in dry ether at room temperature gave **5**, α-chlorotoluene, α-toluenethiol, dibenzyl sulfide, **7**, α,α-di(benzylthio)toluene, and benzyl α-toluenethiolsulfonate.[52] Pummerer[4b] reported that **8** gave α-chlorotoluene and some **5** on treatment with alcoholic hydrogen chloride but that it could be boiled with 50% sulfuric acid with no evidence of thiol. Finally, Hilditch[53] showed that diisoamyl sulfoxide with hydrogen chloride in absolute ethanol gave isoamylthiol and isovaleraldehyde.

It is clear than that the reaction of sulfoxides with hydrogen chloride differs from that with acetic acid in several important aspects. First, with unsymmetrical, activated sulfoxides, there is a much higher specificity of reaction site with acetic acid than with hydrogen chloride. Second, unactivated sulfoxides which are stubborn (**6**) or inert (**8**) in acetic acid react readily with hydrogen chloride. Third, reaction of activated sulfoxides with hydrogen chloride in ether is clean with dithioacetals as the only sulfur-containing product while similar reaction of unactivated sulfoxides gives a profusion of products. In our opinion, it is virtually impossible to reconcile all of these disparities in a unique mechanistic scheme.

The reports of the formation of α-chlorotoluene in the reactions of **6** and **8** in ether–hydrogen chloride aroused the suspicion that chloride ion might be inducing a redox reaction of sulfoxides in place of, or in addition to, the acid-catalyzed process. As a test, **8** was refluxed in acetic acid containing excess lithium chloride. Reaction occurred producing phenyl disulfide *inter alia*.[54]

(50) D. T. Gibson, *J. Chem. Soc.*, 2637 (1931).
(51) J. A. Smythe, *ibid.*, 349 (1909).
(52) Not "dibenzyl disulfoxide" as originally claimed. See P. Allen, Jr., P. J. Berner, and E. R. Malinowksi, *Chem. Ind.* (London), 208 (1963).
(53) T. P. Hilditch, *Ber.*, **44**, 3583 (1911).
(54) Preliminary results of work in progress with R. J. Petsche.

Nucleophilic displacement by chloride ion on the α carbon in protonated sulfoxide could lead to benzylic chlorides and sulfenic acids. These acids are known to disproportionate, eventually producing disulfides and thiolsulfonates. Nucleophilic chloride ion attack could also occur at sulfur[55] in the O-protonated sulfoxide generating a chlorosulfonium species, an intermediate reminiscent of that suggested[56] for the chlorination of benzylic sulfides with N-chlorosuccinimide.

D. The Reaction with Acetic Anhydride.—This reaction has attracted a great deal of attention.[6,57-60] The present state of the mechanistic study has been summarized[6,60] and need not be repeated here. However, it is instructive to consider some of the similarities and contrasts between this reaction and the redox reactions of sulfoxides under other conditions, notably A and C.

First, reaction with acetic anhydride does not require the presence of an activating group. Thus, **6**, **8**, phenylsulfinylmethane, and DMSO all react[57] according to eq 3. No report of the reaction of **1** with acetic anhydride has yet appeared. The specificity (or lack of it) in its reaction should be very helpful in clarifying the relationship(s) among these several redox reactions.

(55) J. L. Kice and G. Guaraldi, *Tetrahedron Lett.*, 6135 (1966).
(56) D. L. Tuleen, *J. Org. Chem.*, **32**, 4006 (1967).
(57) L. Hörner and P. Kaiser, *Ann.*, **626**, 19 (1959).
(58) F. G. Bordwell and B. M. Pitt, *J. Amer. Chem. Soc.*, **77**, 572 (1955).
(59) W. E. Parham and M. D. Bhavsar, *J. Org. Chem.* **28**, 2686 (1963).
(60) S. Oae and M. Kise, *Tetrahedron Lett.*, 1409 (1967).

Again, it was reported[60] that, in a series of *para*-substituted phenylsulfinylmethanes, electron-donating *para* groups facilitated the reaction with acetic anhydride while electron-withdrawing groups retarded it. A similar order has been observed[3,61] for the reaction of *para*-substituted phenylsulfinylacetic acids in acetic acid. No comparable kinetic study for the hydrogen chloride reaction has yet been reported.

Finally, while the reaction in acetic acid of activated sulfoxides is demonstrably acid catalyzed, there has been no clear indication of similar dependence for either the acetic anhydride or the hydrogen chloride reaction.

Therefore, while certain parallels undeniably exist, they are far from exact and should be applied, if at all, with circumspection. Briefly, our conclusion is that much caution should be exercised in applying the putative mechanisms suggested by one substrate under a particular set of conditions to the same substrate under a different set of conditions, let alone to different substrates under different conditions.

Registry No.—2, 21299-21-8; 2 (labeled), 21298-63-5; **3**, 21299-22-9; **4**, 555-16-8; **7**, 150-60-7; **8**, 833-82-9; **10**, 21275-31-0; α,α-di(*p*-nitrobenzylsulfonyl)toluene, 21298-64-6; ethyl α-(*p*-nitrophenylsulfoxide)acetate, 21298-65-7; ethyl α,α-di(*p*-nitrophenylthio)acetate, 21298-66-8; α,α-di(*p*-nitrophenylthio)acetic acid, 2129-867-9; phenyl disulfide, 882-33-7.

(61) M. V. Zeller, M.S. Thesis, John Carroll University, Aug 1966.

The Electrochemical Reduction of Vinyl Bromides

LARRY L. MILLER AND EDWARD RIEKENA[1]

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521

Received November 14, 1968

The electrochemical reduction of triphenylbromoethylene in dimethylformamide at a mercury cathode has been studied. Isolation and characterization of the cathodic products from a controlled potential electrolysis at −2.2 V (*vs.* sce) demonstrated the formation of triphenylethylene and triphenylethane. Gas chromatographic and coulometric analysis showed that at this potential triphenylbromoethylene is cleanly converted into triphenylethylene in a two-electron reduction. This is then followed by conversion of the latter into triphenylethane in a second two-electron step. Reduction at −1.8 V gave only triphenylethylene. Voltammetry with a dropping mercury electrode gave a two-wave polarogram. The half-wave potential of the second wave was the same as that of triphenylethylene, and the data is interpreted as arising from reductive cleavage of the bromide at the first wave followed by reduction of the olefin at the second. A comparison of the first wave, half-wave potentials (*vs.* sce) for triphenylbromoethylene (−1.60), 1,1-diphenyl-2-bromoethylene (−1.80), α-bromostyrene (−1.86), *trans*-β-bromostyrene (−1.98), 1-anisyl-2,2-diphenylbromoethylene (−1.66), 2-anisyl-1,2-diphenylbromoethylene (−1.63), vinyl bromide (−2.46), and 1-methyl-2-bromopropene (>−2.6) is interpreted mechanistically. It is proposed that the rate-determining step is addition of an electron to the lowest vacant π molecular orbital. This is probably followed by loss of bromide from the radical anion, addition of a second electron, and protonation of the resulting vinyl anion. Alternatively, protonation of the radical anion could precede loss of bromide.

In 1949 von Stackelberg and Stracke[2] established that electrochemical reduction converted many alkyl and aryl halides into the corresponding hydrocarbons in a clean, two-electron process. More recently a number of studies have attempted to elucidate the mechanism(s) of this reduction. Many of these studies have utilized correlation of some substituent parameter, *e.g.*, σ and σ^*, with polarographic half-wave potentials and have demonstrated that the transition state for reduction generally has some negative charge. The half-wave potentials of simple primary and secondary halides, for example, correlate with σ^* giving a positive ρ value.[3] Benzylic and aromatic halide reduction potentials also yield a positive ρ value when treated by the Hammett method.[4] Streitweiser[5] has, however, emphasized the stepwise nature of benzyl halide reductions to account

(1) Participant in NSF Research Participation for High School Teachers Program, Colorado State University.
(2) M. von Stackelberg and W. Stracke, *Z. Electrochem.*, **53**, 118 (1949).
(3) F. L. Lambert, *J. Org. Chem.*, **31**, 4184 (1966).
(4) J. W. Sease, F. G. Burton, and S. L. Nickol, *J. Amer. Chem. Soc.*, **90**, 2595 (1968).